

CHEMICAL KINETICS

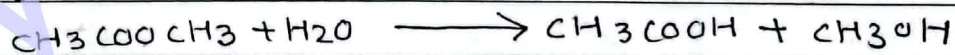
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Introduction:

- A chemical reaction involves the breaking of old bonds and formation of new bonds. In some reactions these processes occur very fast and in some other they occur slow. So the reactions are categorized as slow and fast reaction. For eg:- Neutralization reactions and ionic reactions are fast reaction while rusting is very slow rxn.
- However there are some rxn ~~at~~ which occur with measurable speed and their speeds (rates) can be measured in lab by means of suitable measurable property of the reaction like change in concn, volume, pressure, electrical conductivity, PH etc.
- Following are some examples of chemical rxn's whose speed can be measured.



- Therefore, a branch of chemistry which deals with the rates of chemical reaction, factors affecting rate of chemical reaction and reaction mechanism is called chemical kinetics.



Rate of Reaction

- It tells how fast or slow is the reaction. In simple words it is the speed of reaction.
- It is defined as the change of concentration of either reactant or product per unit time.

$$\text{Rate} = \frac{\text{Change in concentration of reactant or product}}{\text{Time required for change.}}$$

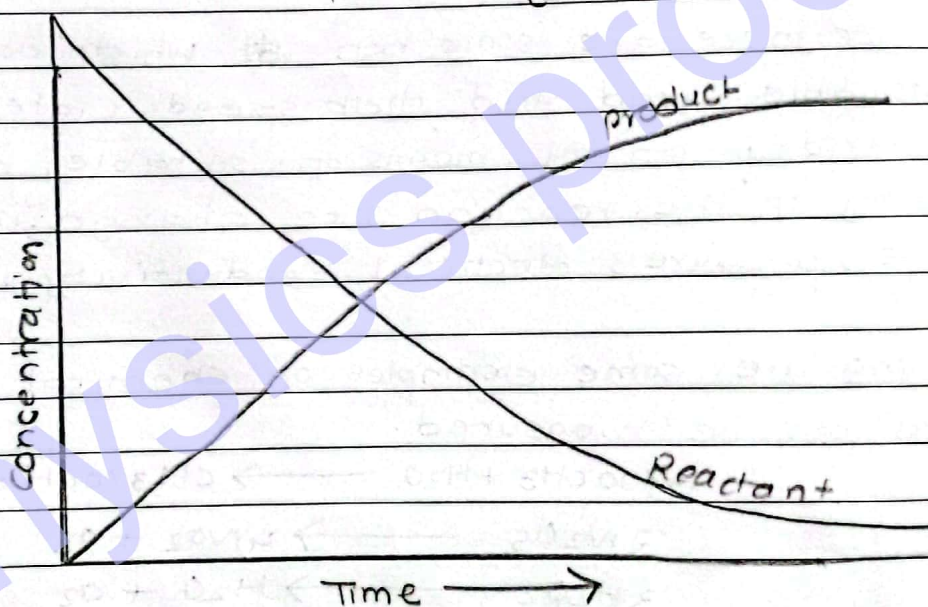


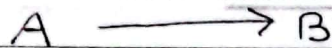
Fig: concentration change of reactants & products with time.

Average Rate of Reaction

- It is defined as rate of change of concentration of either reactant or product at particular interval of time.



Consider a general reaction,



For the given reaction we measure the concentration of A or B at time t_1 and t_2

time	[A]	[B]
t_1	A_1	B_1
t_2	A_2	B_2

→ The rate of rxn with respect of A and B are

$$\text{Rate (A)} = \frac{[A_2] - [A_1]}{t_2 - t_1}$$

$$\text{Rate (B)} = \frac{[B_2] - [B_1]}{t_2 - t_1}$$

$$= - \frac{\Delta A}{\Delta t} \quad (A_1 > A_2)$$

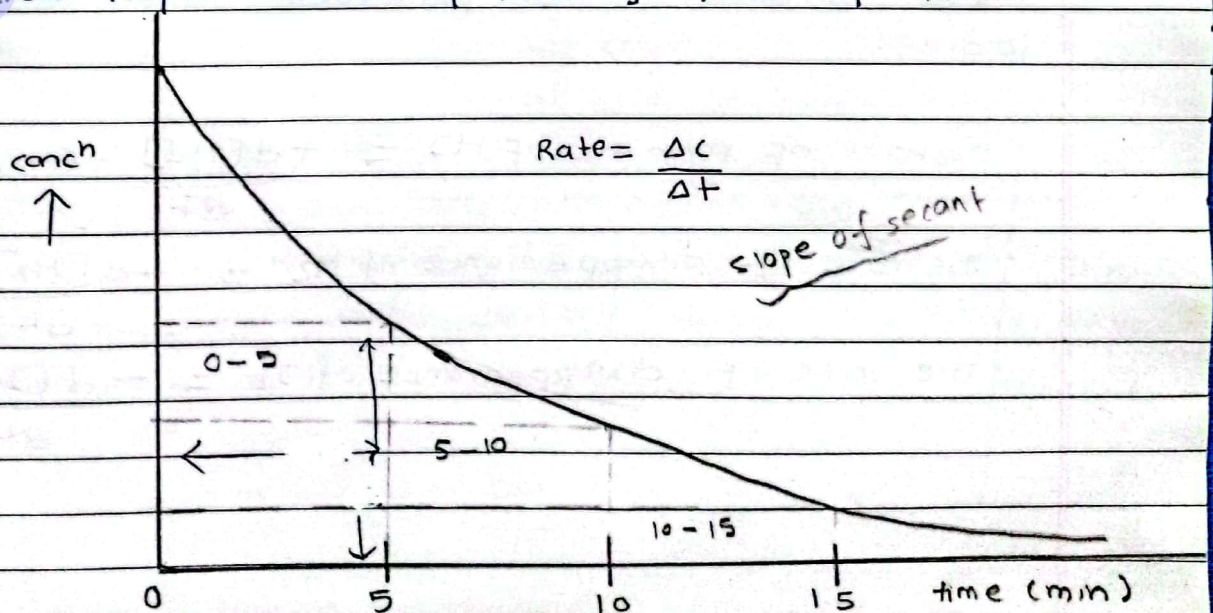
$$= \frac{\Delta B}{\Delta t} \quad (B_2 > B_1)$$

→ The rate of reaction can't be negative, so -ve sign is introduced to make rate positive.

→ The -ve sign in Rate (A) indicates that the concⁿ of reactant is decreasing with time.

→ In rate (B), there is no -ve sign that means $B_2 > B_1$, which means concⁿ of product is increasing

Graphical Representation of Average Rate of Rxn.



Instantaneous rate of reaction

→ It is defined as the rate of change of concentration of either reactant or product at particular instant of time.

→ Average rate of reaction becomes instantaneous when $t_2 \rightarrow t_1$ i.e. $\Delta t \rightarrow 0$.

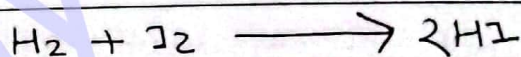
\therefore Instantaneous rate of rxn = $\lim_{\Delta t \rightarrow 0}$ (average rate of rxn)

$$a) \frac{dx}{dt} = - \lim_{\Delta t \rightarrow 0} \frac{\Delta[A]}{\Delta t} = + \lim_{\Delta t \rightarrow 0} \frac{\Delta[B]}{\Delta t}$$

$$= - \frac{d[A]}{dt} = + \frac{d[B]}{dt}$$

For general rxn, $A \rightarrow B$.

Rate of reaction and stoichiometric coefficient



→ Here 1 mole of hydrogen reacts with one mole of iodine to form two moles of hydrogen iodide.

$$\text{The rate of formation of HI} = \frac{+d[HI]}{dt}$$

$$\text{The rate of disappearance of } H_2 = - \frac{d[H_2]}{dt}$$

$$\text{The rate of disappearance of } I_2 = - \frac{d[I_2]}{dt}$$

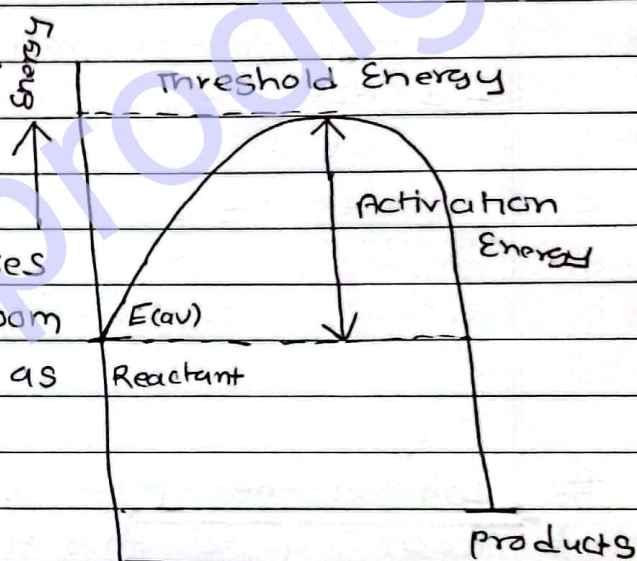
$E_p > E_r \rightarrow$ Absorption of Energy \rightarrow Endothermic
 $E_r > E_p \rightarrow$ Releases Energy \rightarrow Exothermic

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Rate of Formation of HI = 2X rate of disappearance of H₂
= 2X rate of disappearance of I₂

$$\therefore \text{Equivalent Rate of rxn} = + \frac{1}{2} \frac{d[\text{HI}]}{dt} = - \frac{d[\text{I}_2]}{dt}$$
$$= - \frac{d[\text{I}_2]}{dt}$$

Energy Terms:



1) Average Energy [E_{av}]

Every reacting molecules possesses a certain amount of Energy at room temperature which is known as average energy.

2) Activation Energy [E_a]

The minimum amount of Energy that must be associated with reactants to cross the energy barrier and form products is called Activation energy

3) Threshold Energy (E_{th})

It is the minimum amount of energy that must be associated with reactants to cross the energy barrier and form the product. It is the sum of average and activation energy.

$$\therefore E_{th} = E_{av} + E_a$$

Qn) In the rxn $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. If the rate of formation of NO_2 is $2 \times 10^{-4} \text{ mol ltr}^{-1} \text{ sec}^{-1}$ Find the rate of formation of N_2O_5 .

→ Solution:-

Rate of decomposition of N_2O_5

$$\text{Eq rate} = \frac{-1}{2} \frac{d(\text{N}_2\text{O}_5)}{dt} = \frac{1}{4} \frac{d(\text{NO}_2)}{dt} = \frac{d[\text{O}_2]}{dt}$$

Taking first two ratios

$$-\frac{d(\text{N}_2\text{O}_5)}{dt} = \frac{2}{4} \frac{d(\text{NO}_2)}{dt}$$

$$= \frac{1}{2} \times 2 \times 10^{-4}$$

$$= 1 \times 10^{-4} \text{ mol ltr}^{-1} \text{ sec}^{-1}$$

Taking last two ratios

$$\frac{d(\text{O}_2)}{dt} = \frac{1}{4} \frac{d(\text{NO}_2)}{dt}$$

$$= \frac{1}{4} \times 2 \times 10^{-4}$$

$$= 5 \times 10^{-5} \text{ mol ltr}^{-1} \text{ sec}^{-1}$$

Collision theory

- According to this theory, for the formation of product, **collision** of the molecules **is must**.
- Not every collision leads to the formation of product, only **effective collision** gives product.
- For the collision to be effective the **energy must be sufficient**. so that they cross the imaginary energy barrier, and molecules must collide in **proper orientation**.
- This theory assumes molecules as sphere.
- This theory is applicable for bimolecular molecules only.

Remember Bio-collision 😊
te-te.



Factors affecting Rate of reaction:

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No. of collision per unit time is called **collision frequency**.

Rate of reaction & collision frequency.

- ① **Nature of reactant** :- Ionic reactions are fast in nature whereas covalent reactions takes time as old bond need to break and new bond are formed.
- ② **Concentration** :- It is directly proportional to ROR. As the conc^n increases ROR increases and viceversa. When conc^n increases, collision frequency increases and hence rate of rxn increases.
 - Qn) Why rate of rxn is more at beginning?
 - Because conc^n is high at beginning -----
 - Qn) Why most of chemical's are available in powdered form?
 - For a given sample, powdered form has more surface area than that in lumps and hence it helps to increase the Rate of reaction.
- ③ **Surface Area** :- It is directly proportional to ROR. As the surface area increases, the chance of collision increases and then collision frequency increases which lead to increase the rate of rxn.
- ④ **Temperature** :- It is directly proportional to ROR. When temperature increases, the K.E of the molecules also increases, then molecules vibrates fast

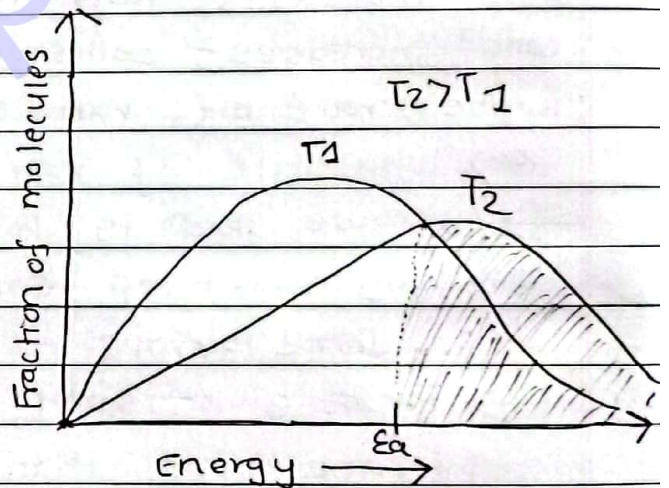
So chance of collision increases, then collision frequency increases and hence rate of reaction increases.

→ For each 10°C rise, ROR increases 2 or 3 times
 2^n or 3^n

Above fact is explained by Temperature coefficient
 $(T_x) = \frac{k_t + 10}{k_t} = 2 \text{ or } 3$ #

Maxwell Energy Distribution curve.

→ It is the curve/graph plot b/w fraction of molecules to the energy associated with them. The graph shows at higher temp. the fraction of collisions with sufficient energy equal to or greater than E_a increases, so ROR also increases.



Arrhenius Equation

→ Svante Arrhenius developed a mathematical relationship between rate constant (k) and temperature

$$k = A e^{-E_a/RT}$$

A → frequency factor

E_a → Activation Energy

R → Universal gas constant.



$$\log k = \log A - \frac{E_a}{RT}$$

(T_1 and T_2)

$\therefore k \propto T$

For two different temp^s, let k_1 and k_2 be their rate constant

Then $\log k_1 = \log A - \frac{E_a}{RT_1}$

$$\log k_2 = \log A - \frac{E_a}{RT_2}$$

$$\log k_2 - \log k_1 = \log A - \frac{E_a}{RT_2} - \log A + \frac{E_a}{RT_1}$$

$$\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 \cdot T_2} \right) \quad \#$$

Catalyst.

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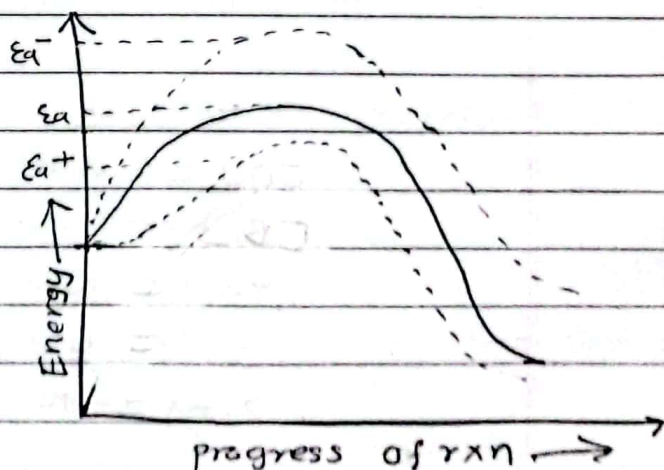
- A substance that alters the rate of reaction without undergoing any chemical change in itself is known as catalyst.
- There are two types of catalyst i) positive catalyst and ii) negative catalyst.
- Positive catalyst like MnO_2 increases the rate of rxn as it lowers the Activation energy and many more molecules can cross the imaginary energy barrier.
- Negative catalyst like glycerol decreases the rate of rxn as they higher's the activation energy.

Here,

E_a = activation energy

E_a^+ = activation energy with +ve catalyst

E_a^- = activation energy with negative catalyst.



Light :- photochemical rxn's only takes place in presence of light. For such reactions, Intensity of light \propto ROR

Rate law VERY IMP

- It explains the dependence of rate of rxn (ROR) on concn of species in reaction in which each concn term appears with certain power.
- This dependence is very complex as it changes with change in concn of species.
- Here, we only study the simplest form of dependence i.e. by conducting experiments.

EG:- $2A + 3B \rightarrow \text{product}$

If [A] double ROR \rightarrow double
 If [B] double ROR \rightarrow 4 times
 Then ROR \propto [A]¹ ROR \propto [B]²
 $\therefore \text{ROR} = k [A]^1 [B]^2$ #

In general term,

$\text{ROR} = k [A]^x [B]^y$

where k = rate constant

[A] = concn of A

[B] = concn of B

x = order of rxn w.r.t A [vestive, 0, frac]

y = order of rxn w.r.t B

x+y = overall order of rxn (n)



Rate Constant / Velocity constant / specific rxn rate (K)

we have,

$$ROR = k [A]^x [B]^y$$

If $[A] = [B] = 1$ (unity) ^{mol L⁻¹}. Then

$$ROR = k$$

Thus **rate constant is defined as** the rate of rxn when the concentration of all the reactants is taken unity.

Unit of Rate constant (K)

we have $ROR = k [A]^x [B]^y$

$$k = \frac{ROR}{[A]^x [B]^y} \quad \text{--- (1)}$$

$$\text{or } k = \frac{\text{mol L}^{-1} \text{ sec}^{-1}}{(\text{mol L}^{-1})^x (\text{mol L}^{-1})^y}$$

$$\text{or } k = \frac{\text{mol L}^{-1} \text{ sec}^{-1}}{(\text{mol L}^{-1})^{x+y}} \quad (x+y = n)$$

$$\text{or } k = (\text{mol L}^{-1})^{1-n} \text{ sec}^{-1} \quad \#$$

Characteristics of Rate constant.

- It is specific to the rxn.
- It is dependent on temperature.
- It is independent of concⁿ as the ratio of (1) always remains constant.
- It measures Rate of Rxn (ROR)
- It's unit^s dependent on order of rxn.
- Different rxn have different values of rate const. So it is specific to the rxn.



$$\text{unit of } k = (\text{mole L}^{-1})^{1-n} \text{ sec}^{-1}$$

order of rxn (n)	units of k
0 (zero order rxn)	$\text{mole L}^{-1} \text{ sec}^{-1}$
1 (First " ")	sec^{-1}
2 (second " ")	$\text{mole}^{-1} \text{ L sec}^{-1}$

and so on.

Qn) For $2A + B \rightarrow \text{products}$
 when $[A]$ is doubled alone, ROR increased by 2
 when $[A]$ & $[B]$ both are doubled, ROR increase by 8 times. Write rate law expression, find order of rxn.

→ we have,

$$\text{ROR} = k [A]^x [B]^y$$

$x=1$ ($[A]$ double, ROR double)

$$2 \text{ ROR} = k [2A]^x [B]^y \quad \text{--- (1)}$$

($x=1$)

When both doubled,

$$8 \text{ ROR} = k [2A]^1 [2B]^y$$

$$8 \text{ ROR} = k [2A]^1 [2B]^y \quad \text{--- (2)}$$

when (2) \div (1) we get

$$4 = \frac{[2B]^y}{[B]^y} = 2^y$$

$$2^y = 4 = (2)^2$$

$$\therefore y = 2$$

So rate law expression is,

$$\text{ROR (Y)} = k [A]^1 [B]^2 \quad \#$$

$$\text{Order of rxn} = x + y = 1 + 2 = 3$$

3rd order of rxn.

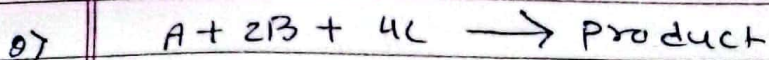


RORX K.

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When volume of container is double d, ROR decreases 8 times. When $[A] \rightarrow$ doubled $[B] \rightarrow$ halved, ROR increases 4 times

When $[C]$ increases 4 times ROR increases 64 times

Find rate law expression and order of reaction.

\rightarrow when vol of container is doubled

$$[A] = \frac{[A]}{2} \quad [B] = \frac{[B]}{2} \quad [C] = \frac{[C]}{2}$$

General term, $ROR = k [A]^x [B]^y [C]^z$ — (1)

$$\frac{1}{8} ROR = k \left[\frac{[A]}{2}\right]^x \left[\frac{[B]}{2}\right]^y \left[\frac{[C]}{2}\right]^z$$
 — (2)

(1) \div (2) we get $8 = 2^x \cdot 2^y \cdot 2^z = 2^{(x+y+z)}$

$$x+y+z = 3$$
 — (3)

case 2 \gg

$$4 ROR = k [2A]^x [2B]^y [C]^z$$
 — (4)

Dividing (4) by (1) we get

$$4 = 2^x \cdot 2^y \Rightarrow 2^{(x+y)}$$

$$x+y = 2$$
 — (5)

From (3) and (5) we get,

$$z = 3 - 2 = 1 \checkmark$$

case 3 \gg

$$64 ROR = k [A]^x [B]^y [4C]^z$$
 — (6)

Dividing (6) by (1) we get

$$64 = 4^z \Rightarrow [4]^3 = [4]^z$$

$$\therefore z = 3 \checkmark$$

$$x+y+z = 3$$

$$x+y+3 = 3$$

$$x+y = 0 \quad (*)$$

$$x-y = 2 \quad (*)$$

$$2x = 2 \Rightarrow x = 1$$

$$y = 3 - x - z$$

$$= 3 - 1 - 3 = -1$$



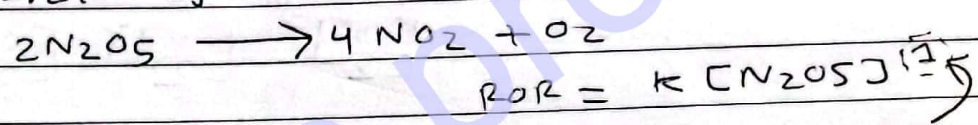
So required rate expression is

$$R_{OR}(v) = k [A]^1 [B]^{-1} [C]^3$$

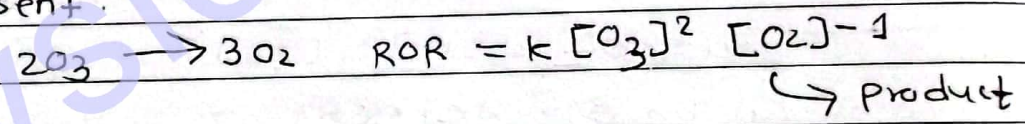
order of rxn = $x + y + z$
 $= 1 - 1 + 3 = 3 \checkmark$
 third^{order} of rxn

Some important points about order of rxn.

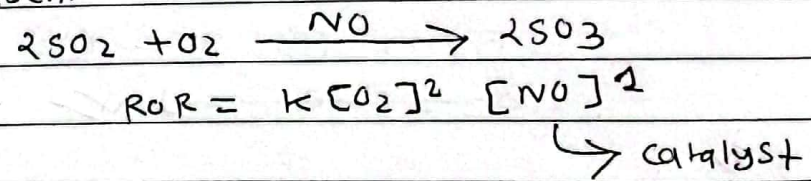
<1> stoichiometric coefficients have nothing to do with order of rxn.



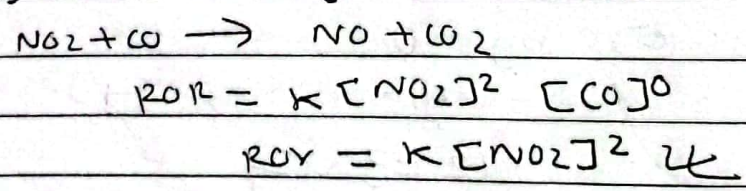
<2> In rate law, concentration terms of products can be present.



<3> In rate law, concentration term of some catalyst may be present



<4> In rate law, concn term of some reactant may be absent



Simple Elementary single Step Reaction.

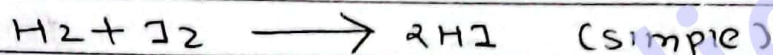
→ Law of mass action may be valid in some rxn



$$ROR = k [x]^2 [y]^3$$

If and only if rxn is simple and single step

Eg:-



$$\text{Then } ROR = k [H_2]^1 [I_2]^1 \quad \times$$

(Guldberg & Waage law of mass action)

Rate of reaction

- It is the change in the concentration of either reactants or product.

- It depends on concentration of reactants

- It decrease with progress of time.

Rate constant of reaction

- It is the proportionality constant of rate law expression.

- It does not depend on concentration of reactants

- It remains constant and is independent of the progress of the rxn.

Order of Reaction

Let us consider a general reaction



Then rate law of the reaction is

$$\text{Rate} = k [A]^x [B]^y$$

where x and y are constant numbers. They are known as the order of reaction with respect to A and B respectively. Then the overall order of reaction is $m+n$.

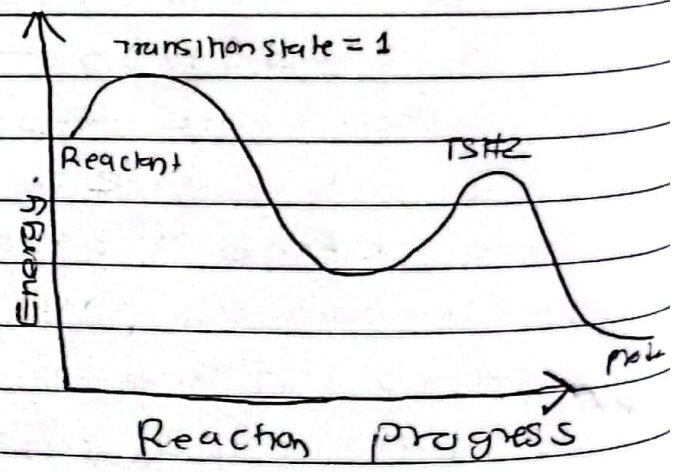
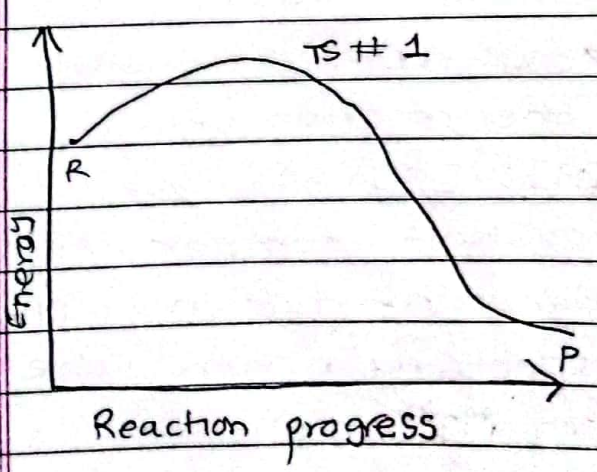
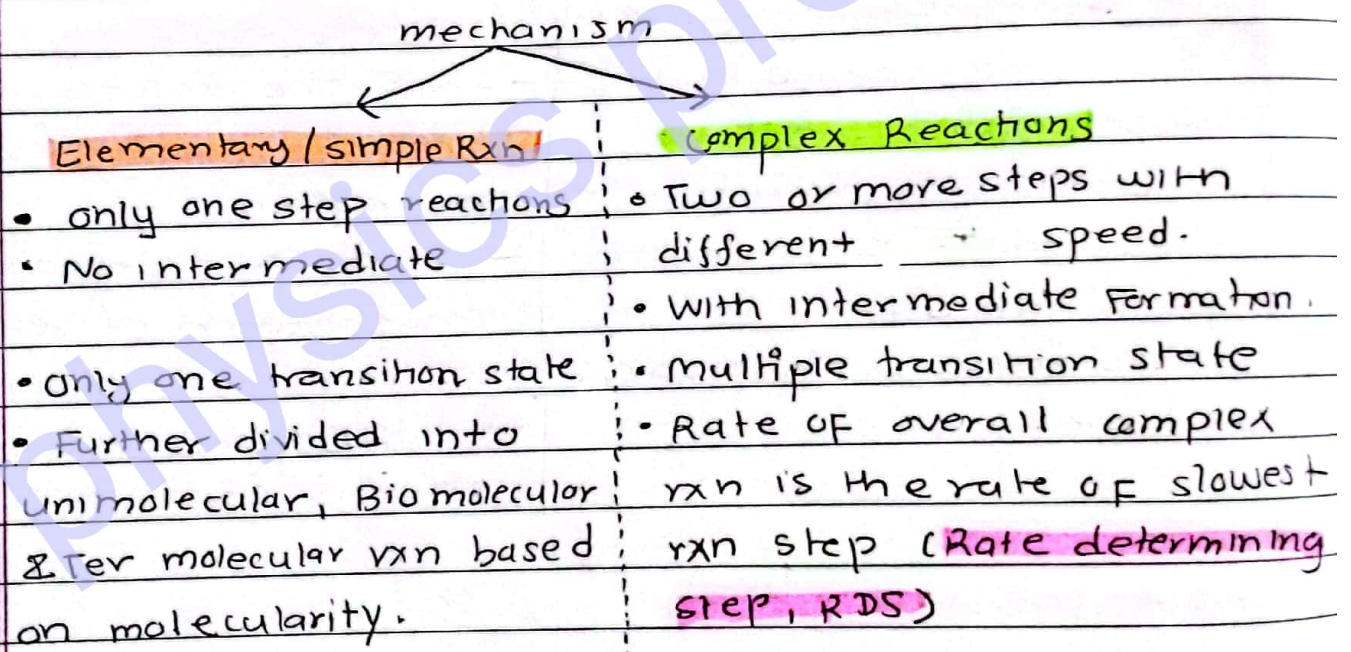


→ Thus, the order of reaction is defined as the sum of all the power of the concentration terms in the rate equation.

→ It indicates the degree in which the rate depends on the concentration of that particular reactant.

Molecularity of Reaction:

→ Reactions can be divided on the basis of reaction mechanism



Total no. of reacting species which collide simultaneously to bring product is called **molecularity**.

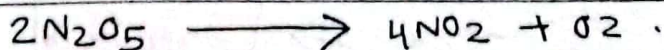
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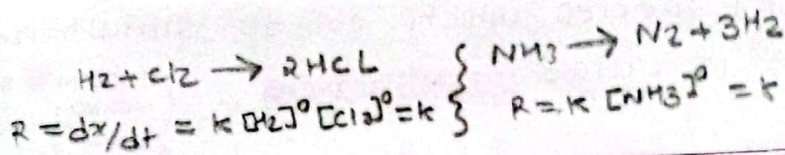
For elementary or simple reaction.

- Reaction completes in only one step.
- It can be determined from the sum of stoichiometric coefficient of the balanced chemical equation.
- Molecularity and order of rxn are same for the simple reaction. Here unimolecular rxn is first order and bimolecular rxn is second order and so on.

For Complex reaction

- Reaction completes in more than one step.
- Each step is elementary reaction. The overall reaction is obtained by adding all the elementary steps.
- These elementary steps give the detail description about the reaction. So they are called mechanism of the reaction.
- These various elementary steps have different rates. Some of the steps are fast and some are slow.
- The overall rate of the reaction is determined by the step whose rate is the slowest. Therefore, the slowest reaction is known as rate determining step (RDS).
- Molecularity of the complex reaction is determined from the number of reacting species ~~having~~ involving in the rate determining step. For complex reaction, the number of reacting species present in the rate determining step is the **molecularity of the complex reaction**.

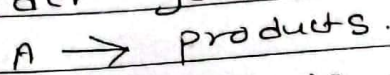




Zero-order reaction:

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→ In zero order rxn, the rate of reaction is independent of concentration of reactants. Let us consider general zero-order reaction

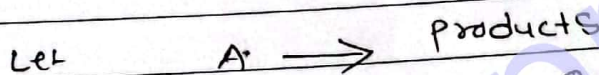


The rate law for this is

$$\text{Rate} = k[A]^0$$

Then, $\frac{d[A]}{dt} = k_0$

Differential rate eqn?
 $x = kt$
 $y = mx + c$



Initially $a \text{ mol l}^{-1}$

After time t $(a-x)$

Then, $\frac{dx}{dt} = k_0 \cdot (a-x)^0$

$$dx = k_0 dt$$

on integrating

$$\int dx = \int k_0 dt$$

$$x = k_0(t) + I$$

where I is integrating constant

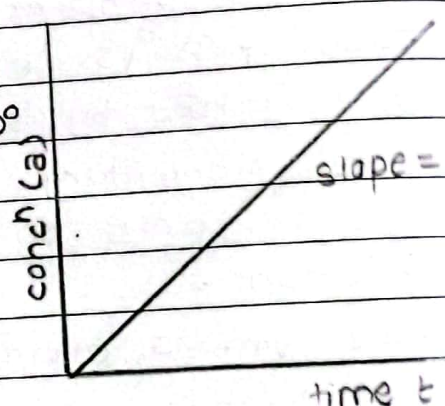
when $t=0$, $x=0$.

$$\therefore I = 0$$

$$\text{so, } x = k_0 t$$

$$k_0 = \frac{x}{t}$$

integrated rate eqn of zero order rxn
 $x = k_0 t$



Half life

$t = t_{1/2}$, $x = a/2$

$$k_0 = \frac{a/2}{t_{1/2}}$$

$$t_{1/2} = \frac{a}{2k_0}$$

$$t_{1/2} \propto a$$



ALL decomposition rxn are 1st order rxn

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First order rxn

	A	→	Products
Initial	a		0
Final (t)	(a-x)		x

* Rate depends on
first power of
concn terms or only
one concn terms.

$$R \propto A^1 \quad (\text{for first order})$$

$$R = k A^1$$

$$\frac{dx}{dt} = k(a-x) \quad [\text{differential rate eqn}]$$

$$\frac{dx}{(a-x)} = k dt$$

on integrating we get

$$-\ln(a-x) = k_1 t + I \quad \text{--- (1)}$$

where I is Integrating constant.

initially $x=0$ and $t=0$.

so, $-\ln(a) = I$. so eqn (1) becomes.

$$-\ln(a-x) = k_1 t - \ln a.$$

$$k_1 t = -\ln(a-x) + \ln a.$$

$$k_1 t = \ln \left(\frac{a}{a-x} \right)$$

$$k_1 = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right) \quad [\because \ln = \frac{2.303}{100}]$$

Half life

[Integrated rate eqn]

$$x = a/2 \quad t = T_{1/2}$$

$$k_1 = \frac{2.303}{T_{1/2}} \log \left(\frac{a}{a-a/2} \right)$$

$$T_{1/2} = \frac{2.303}{k_1} \log \left(\frac{2a}{a} \right)$$

$$T_{1/2} = \frac{0.693}{k_1}$$



#

Graphical Representation of first order rxn.

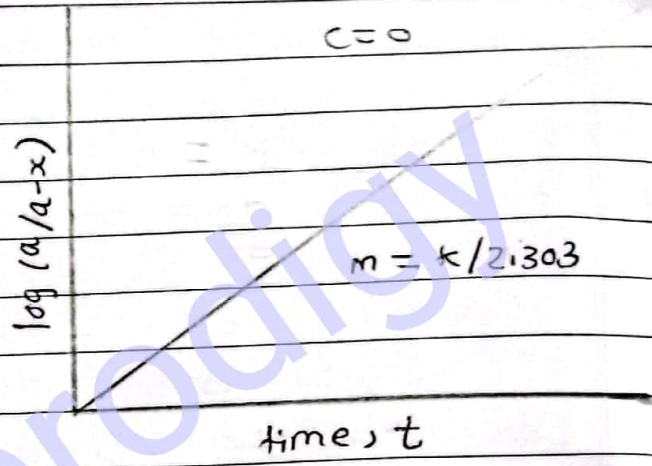
Integrated eqn is,

$$kt = 2.303 \log \left(\frac{a}{a-x} \right)$$

Rearranging eqn

$$\log \left(\frac{a}{a-x} \right) = \frac{k}{2.303} t$$

$$y = mx + c$$



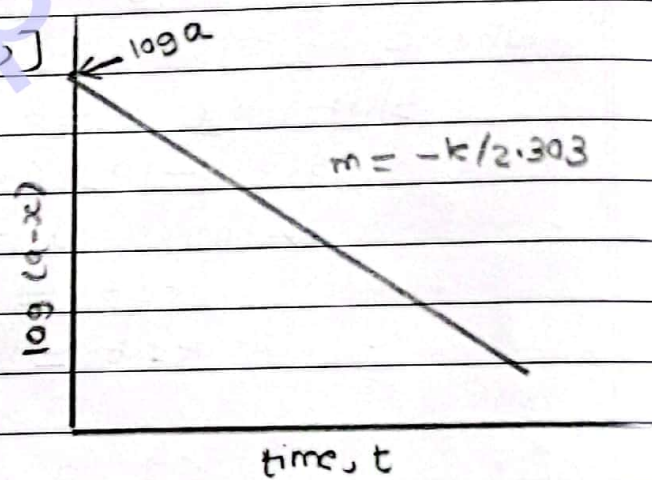
Also,

$$kt = 2.303 [\log a - \log (a-x)]$$

$$\frac{k}{2.303} t = [\log a - \log (a-x)]$$

$$\log (a-x) = -\frac{k}{2.303} t + \log a$$

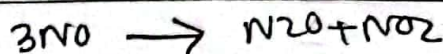
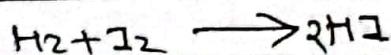
$$y = mx + c$$



Second-order reaction.

→ The rxn whose rate is determined by change of two concn terms (m+n=2) is called the second order rxn.

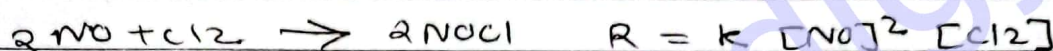
$$\text{Rate} = \frac{dx}{dt} = k[A]^2 \quad | \quad k[A][B]$$



Third order Rxn

→ The rxn which is dependent in three concn terms.

$$R = \frac{dx}{dt} = k[A]^3 / k[A][B][C] / k[A]^2[B]$$



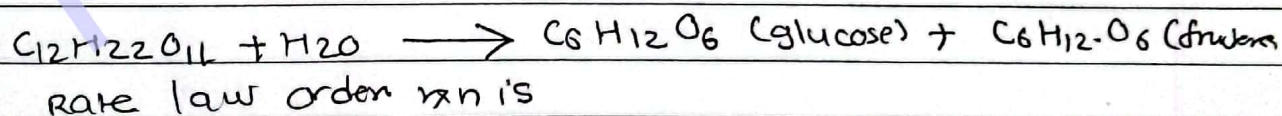
Pseudo Order Rxn

→ Higher order reaction which follows lower order kinetics is called pseudo order rxn.

→ If higher order rxn follows first order kinetics then rxn is called pseudo-first order rxn.

→ When one of the reacting species is present in large excess in the reaction. The ROR is independent of concn of the species.

Let us consider hydrolysis rxn of cane sugar.



$$\text{rate} = k[C_{12}H_{22}O_{11}][H_2O]$$

This rxn seem to follow 2nd order but if large excess of water is taken then amount of



$k =$

9n) A first order rxn has rate constant 1.3×10^{-3} per sec. How long does this rxn take to finish 60% of the rxn?

→ Let the first order rxn be,



$$t=0 \quad a=100\% \quad x=0$$

$$t=? \quad (a-x) = (100-60)\% \quad x=60\% \\ = 40\%$$

For first order rxn:

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$1.3 \times 10^{-3} = \frac{2.303}{t} \log \left(\frac{100}{40} \right)$$

$$\therefore t =$$

② A rxn has rate constant 0.005 per minute. How long does it take to complete 90% of the rxn?

→ Here, the rate constant is 0.005 per min so ~~the~~ it is first order rxn.



for first order rxn, completes in infinite time.

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- ⑤ A first order rxn has half life period 30 minute. How long does this rxn take to finish 87.5% of the rxn?

→ Here, $T_{1/2} = 30 \text{ min}$,

$$\text{Now, rate constant } (k) = \frac{0.693}{T_{1/2}}$$

$$= \frac{0.693}{30 \text{ min}}$$

$$= 0.0231 \text{ per min.}$$

Let the first order rxn be,



$$t=0 \quad a=100\% \quad x=0$$

$$t=? \quad (a-x)=100-87.5\% \quad x=87.5\% \\ =12.5\%$$

Now we have

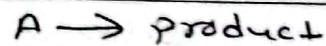
$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$0.0231 = \frac{2.303}{t} \log \left(\frac{100}{12.5} \right)$$

$$t = 90 \text{ minutes.} \quad \text{ans}$$

- ④ A first order rxn takes 20 min to complete 80% of the rxn. How long does the same rxn takes to complete 95% of the rxn.

→ Let the first order rxn be,



$$t=0 \quad a \quad 0$$

$$100\% \quad 0$$

$$t=20 \text{ min} \quad 20\% \quad 80\%$$

$$5\% \quad 95\%$$

$$\text{Now } k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$t = \frac{2.303}{0.011} \log \left(\frac{100}{5} \right)$$

$$= \frac{2.303}{20} \log \left(\frac{100}{80} \right) = 0.011 \text{ per min.}$$

$$= 268 \text{ min.}$$



$$(\text{mol l}^{-1})^{1-n} \text{sec}^{-1}$$

5) A first order rxn has rate constant 0.03 per sec. If the initial concn of reactant is 2 mol per ltr. How long does it take to form 0.75 mol ltr⁻¹ of product.

→ Here, $k = 0.03$ per sec

$$a = 2 \text{ mol ltr}^{-1}$$

$$x = 0.75 \text{ mol ltr}^{-1}$$

$$a-x = (2-0.75) = 1.25 \text{ mol ltr}^{-1}$$

$$\text{Now, } t = \frac{2.303}{k} \log \left(\frac{a}{a-x} \right)$$

$$= \frac{2.303}{0.03} \log \left(\frac{2}{1.25} \right) = 15.66 \text{ per sec.}$$

6)



Exp. NO.	[Cl ₂]	Initial rate
1	0.02	2.4×10^{-4}
2	0.02	2.16×10^{-3}
3	0.04	4.32×10^{-3}

Determine:-

i) order of rxn w.r.t to Cl₂ and NO and overall

ii) If [Cl₂] = 0.5 mol l⁻¹ & [NO] = 0.4 mol l⁻¹

what is rate?

→ let the rate law eqn be:

$$\text{Rate} = k [\text{Cl}_2]^m [\text{NO}]^n \quad \text{--- (2)}$$

From given data

$$2.4 \times 10^{-4} = k [0.02]^m [0.02]^n \quad \text{--- (2)}$$

$$2.16 \times 10^{-3} = k [0.02]^m [0.03]^n \quad \text{--- (3)}$$

$$4.32 \times 10^{-3} = k [0.04]^m [0.03]^n \quad \text{--- (4)}$$



$$(\text{mol L}^{-1})^{1-3} \text{ sec}^{-1}$$

$$\text{mol}^{-2} \text{ L}^2 \text{ sec}^{-1}$$

Dividing (ii) by (iii) we get.

$$\frac{2.4 \times 10^{-4}}{2.16 \times 10^{-3}} = \frac{(0.01)^n}{(0.03)^n}$$

$$\text{or } \frac{1}{9} = \left(\frac{1}{3}\right)^n \Rightarrow \left(\frac{1}{3}\right)^2 = \left(\frac{1}{3}\right)^n$$

$$\therefore n = 2 \checkmark$$

Dividing (iii) by (iv) we get

$$\frac{2.16 \times 10^{-3}}{4.32 \times 10^{-3}} = \frac{(0.02)^m}{(0.04)^m}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^m \Rightarrow \therefore m = 1 \checkmark$$

Hence the order of rxn w.r.t Cl_2 is 1st and w.r.t NO is 2nd. And overall is 3rd.

Putting the value of m and n in eqn (i) we get

$$2.4 \times 10^{-4} = k [0.02]^1 \cdot [0.02]^2$$

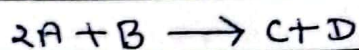
$$\therefore k = \frac{2.4 \times 10^{-4}}{8 \times 10^{-6}} = 30 \cdot \text{mol}^{-2} \text{ L}^2 \text{ sec}^{-1}$$

If $[\text{Cl}_2] = 0.5$ and $[\text{NO}] = 0.4 \text{ mol L}^{-1}$

$$\begin{aligned} \text{Then Rate} &= k [\text{Cl}_2]^m [\text{NO}]^n \\ &= 30 [0.5]^1 [0.4]^2 \\ &= 2.4 \text{ mol/sec} \end{aligned}$$



Q2) The following rate data are obtained at 303 K for the reaction



EXP	[A] mol L ⁻¹	[B] mol L ⁻¹	Initial rate of formation of [D] in mol L ⁻¹
1	0.1	0.1	6×10^{-3}
2	0.3	0.2	7.2×10^{-2}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.4×10^{-2}

Find order of rxn and value of k.

Let the rate law equal be

$$\text{Rate} = k [A]^x [B]^y \quad \text{--- (1)}$$

From given data,

$$6 \times 10^{-3} = k [0.1]^x [0.1]^y \quad \text{--- (2)}$$

$$7.2 \times 10^{-2} = k [0.3]^x [0.2]^y \quad \text{--- (3)}$$

$$2.88 \times 10^{-1} = k [0.3]^x [0.4]^y \quad \text{--- (4)}$$

$$2.4 \times 10^{-2} = k [0.4]^x [0.1]^y \quad \text{--- (5)}$$

Dividing eqn (3) by (4) we get,

$$\frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \left(\frac{0.2}{0.4}\right)^y$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^y \Rightarrow \left(\frac{1}{2}\right)^y = \left(\frac{1}{2}\right)^2$$

$$\therefore y = 2 \quad \checkmark$$

Dividing eqn (2) by (5) we get

$$\frac{6 \times 10^{-3}}{2.4 \times 10^{-2}} = \left(\frac{0.1}{0.4}\right)^x \Rightarrow x = 1 \quad \checkmark$$

\therefore order with respect to A is 1 and B is 2.

overall order = $x + y = 1 + 2 = 3$

\therefore rxn is of 3rd order,

putting value of x and y we get, in eqn (1)

$$6 \times 10^{-3} = k [0.1]^1 \cdot [0.1]^2$$

$$\therefore k = 6 \times 10^{-3}$$

e) What will be the initial rate of rxn if its rate constant is $1 \times 10^{-3} \text{ min}^{-1}$ and the concn of reactant is 2 mol L^{-1} ? How much the reactant will be converted into product in 500 min?

\rightarrow Given, Let rxn be $A \rightarrow \text{Product}$,

$$\text{Rate constant } (k) = 1 \times 10^{-3} \text{ min}^{-1}$$

since unit of k is in min^{-1} so the order of rxn is 1st order.

$$\text{concn of reactant } [A] = 0.2 \text{ mol L}^{-1}$$

$$t_{1/2} = \frac{0.693}{k}$$

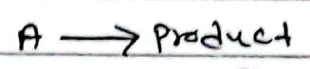
we know first order rxn,

$$R = k [A]^1 =$$

$$= 1 \times 10^{-3} \times (0.2)$$

$$= 2 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1} \quad \#$$

Now, we have



$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$a (0.2) \quad 0$$

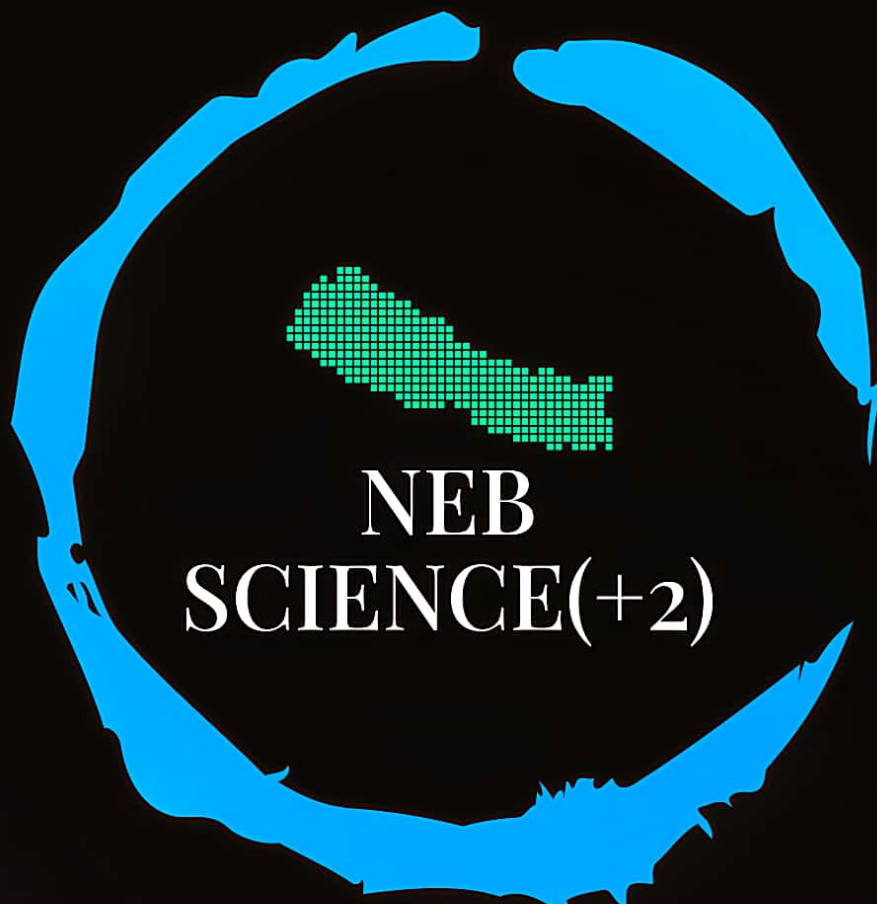
$$a-x \quad x$$

$$1 \times 10^{-3} = \frac{2.303}{500} \log \left(\frac{0.2}{0.2-x} \right)$$

$$(0.2-x)$$

$$\therefore x = 0.0782 \text{ mol L}^{-1}$$





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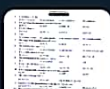
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